JOURNAL OF MATERIALS SCIENCE 5 (1970) 862-868

Dislocations and Twins in Czochralski-Grown Gallium Phosphide Single Crystals

D. LAISTER,* G. M. JENKINS
Department of Metallurgy, University College of Swansea, Glamorgan, Wales

An etching and electron microscopy study has been carried out on {111} oriented slices of gallium phosphide (GaP) taken from Czochralski-grown ingots. The correlation of the etched structure with substructural defects as revealed by transmission electron microscopy has been determined. It has been found that GaP grown by this technique has a high dislocation density and exhibits polygonisation and mechanical twinning. It is found that there is a one-to-one correspondence between surface etch pits and grown-in and mechanically induced dislocations. Stacking faults are also revealed in the etching studies and are shown to be twins in the matrix of the {111} ⟨112⟩ type. It is proposed that the twinning occurs due to the severe growth conditions and may arise by dissociation of dislocations in the sub-boundaries.

1. Introduction

A good deal of interest has been generated in the semiconductor gallium phosphide since the development of a high pressure Czochralski single crystal puller has enabled large single crystals of this compound to be produced in a fairly routine manner [1]. Certain of these bulk ingots have been characterised by a high dislocation density and high twin density [2], the latter causing a large portion of the ingot to be unusable for epitaxial growth and subsequent device application. Since an understanding of the nature of the defect substructure is germane to the production of better material, a characterisation study of the various defects occurring in Czochralski-grown GaP has been made, using etching and transmission electron microscopy techniques.

In previous etching studies [3, 4] some controversy has arisen concerning the correlation of dislocations with etch pits produced by a warm aqua regia solution on {111} oriented samples. It will be shown in this paper that there is a one-to-one correspondence between dislocations emergent on a Ga {111} face and etch pits produced by aqua regia. It has been suggested [5] that the reagent aqua regia is too rapid in its action when used hot and that the addition of modifying agents such as heavy metal ions is needed to retard the reaction rate and thereby preferentially reveal the dislocation arrangement. It will become clear in the following sections on etching that such metal ion additions are not prerequisite for preferential attack of dislocations in Czochralski-pulled GaP.

Some confusion has occurred using etching techniques alone for revealing dislocations in semiconductor crystals particularly with respect to traces running parallel to the surface of the sample [6]. Dislocation traces are produced on crystal faces because contaminants scratch the surface during polishing. Previous work on the III-V semiconductor GaAs [7, 8] has shown that in this material etch-traces are produced on a surface by the passage of some particle of contaminant, causing small dislocation loops to be punched into the matrix of the crystal. These traces are the result of preferential etching of many small dislocation loops produced by the surface damage. Evidence is presented here of a similar phenomenon that occurs in GaP during polishing procedures.

Twinning in semiconductor crystals is not an uncommon occurrence. Microtwins have been observed in silicon [9] and in gallium arsenide [10], where they are produced as a result of poor

---

*Now at Department of Metallurgy, Queen's University, Kingston, Ontario, Canada substrate preparation prior to epitaxial growth, and also in GaP [4]. These were growth twins and as such were characterised by coherent interfaces. Growth twins also occur in Czochralski-pulled GaAs [11] and have been found to be suppressed by change of growth conditions; it was found that good single crystal ingots could be obtained from a non-stoichiometric As-rich melt. It will be seen in the following sections that non-stoichiometry plays a part in the formation of the substructure during growth of GaP.

Face-centred cubic structures are not ordinarily considered to deform by mechanical twinning since the {1 1 1} planes are also the slip planes; however, mechanical twins have been found under extreme conditions [12]. Because of the nature of its crystal structure GaP may be considered to be made up from two interpenetrating face-centred cubic lattices and thus to behave under deformation conditions in a similar manner to simple fcc systems, as do other semiconductor crystals [13]. For this reason mechanical twins forming in GaP are expected to do so only under extreme conditions. Crystals with related lattice structures, GaSb, InSb, Ge and Si, have shown twinning on {1 1 1} planes caused by indentation at high temperatures [14]. The present results show that mechanical twins can form in GaP under the extreme conditions experienced by the crystal during Czochralski growth.

2. Experimental

{1 1 1}-oriented GaP samples were selected from different parts of the bulk-grown ingots and polished on both sides, finishing with $\frac{1}{4}$ μm grade diamond compound reducing them to a final thickness of 0.1 cm. The compositions by volume of the chemical reagents used in the etching studies were as given in the table; all reagent constituents were high grade chemicals.

For the electron microscope examination of GaP, 2.3 mm specimens were ultrasonically cut to fit the microscope specimen holder and polished to 0.05 cm thickness. In the study of etch-pit dislocation correlation the electron microscope specimens were given a brief etching in the various reagents under test, such that etch pits on the Ga {1 1 1} face were only just detectable at 400 × magnification in the light microscope; an etching time of the order of 5 sec was usually sufficient to meet this condition with reagent 1; longer times were needed for reagents 2 and 3. The preparation of foils in GaP suitable for electron transmission was carried out using the Biederman and Brack [15] reagent** which they described for GaAs. Each {1 1 1} oriented GaP disc was thinned from the P($\bar{1}\,\bar{1}\,\bar{1}$) face by dripping the reagent on to the face *via* a glass capillary. In order that the Ga(1 1 1) face was not attacked by the thinning reagent, which produces etch pits on this face, the discs were mounted on glass slides using Lacomit with the Ga(1 1 1) face in contact with the glass plate. The rate of thinning is slow using this reagent, taking about 20 min to perforate a disc.

3. Results

3.1. Etching

Reagent 1 produced well-defined etching features as can be seen in fig. 1a. These features consisted of triangular pits of a symmetrical or asymmetrical nature, depending upon the exact orientation of that portion of the crystal containing the etch pits with respect to the ⟨1 1 1⟩ normal to the plane of observation. Careful examination of the micrograph in fig. 1a shows that the crystal is subdivided by grain boundaries; it will be shown by electron transmission that these are low-angle boundaries and that in this portion of the crystal polygonisation had taken place. A third feature is the etch-channels that are characteristic of stacking faults in this type of material [10, 4]. These faults were slightly misoriented with respect to neighbouring sets in adjacent subgrains because of the polygonisation.

TABLE

Reagent	Composition (v/v)	Comments
1	6HNO_3, 2HF, 1HCl	Well defined etch pits on Ga {111} faces do not produce pits on P{111}; delineates twins on both faces.
2	4HCl 1HNO_3	Produces pits on Ga {111} face only
3	3HCl 1HNO_3*	Ga {111} etch pits, delineates twins.
4	1HF 1HNO_3	Pits not well defined; delineates twins, polygonal boundaries well defined.

*Aqua regia.

**Suggested by A. Brown, Plessey Co, Towcester, Northants

Reagent 1 also revealed the faults on the P{1 1 1} face of a slice (compare figs. 1b, 1c). Reasonably well-defined structures are obtained with reagent 1 at 25° C after 5 min. Finally, shallow channels are seen traversing the slice from one edge of the specimen to the other, being undeviated by polygonisation. High magnification revealed these channels to be made up of shallow pits resembling etch pits of the type formed after dislocations have been etched away [8], only the symmetry of the pits varied from one subgrain to another. These channels will later be shown to be made up from parallel dislocation loops – the results of surface damage.

The faults revealed by etching were determined, using the Laue X-ray back-reflection technique, to lie along the {1 1 0} directions in the {1 1 1} surface; the acute angle between two adjacent sets of twins in the same subgrain was 60°. These faulted regions, which in a later section will be shown to be twinned material, appear to have one end common with a subgrain boundary.

Reagents 2 and 3 both revealed the same features observed after etching a slice with reagent 1. Both these etchants were used at 25° C, reagent 3 producing the etch channels as did reagent 1; however, reagents 3 and 2 took considerably longer to produce a well-defined structure, approximately 15 to 20 min respectively. Reagent 4 produced the structure shown in fig. 1d. Etch pits were not well-defined with this reagent; however, the effect of change of orientation in the twinned regions was quite marked: notice the apparent enhancement of surface damage within a twin.

A routine examination of slices selected from the seed end of an ingot revealed a high dislocation density (evidenced by etch pits at a density of about 10^5 lines/cm^2) and freedom from polygonisation and twinning. Further towards the tail end of an ingot there was evidence of slip having taken place; evidence of alignment of dislocations was also found (see fig. 1e). It is useful to compare this micrograph with that in fig. 1f, which was produced with aqua regia immediately after lapping with 6 μm alumina compound; in fig. 1e there is no gross surface damage effect to mask the substructure, whereas there is such masking in fig. 1f. Twins were present only in the part of the crystal that had polygonised; here the overall dislocation density was estimated at 10^7 lines/cm^2.

3.2. Electron Microscopy

3.2.1. Etch Pits, Surface Damage and Sub-boundaries

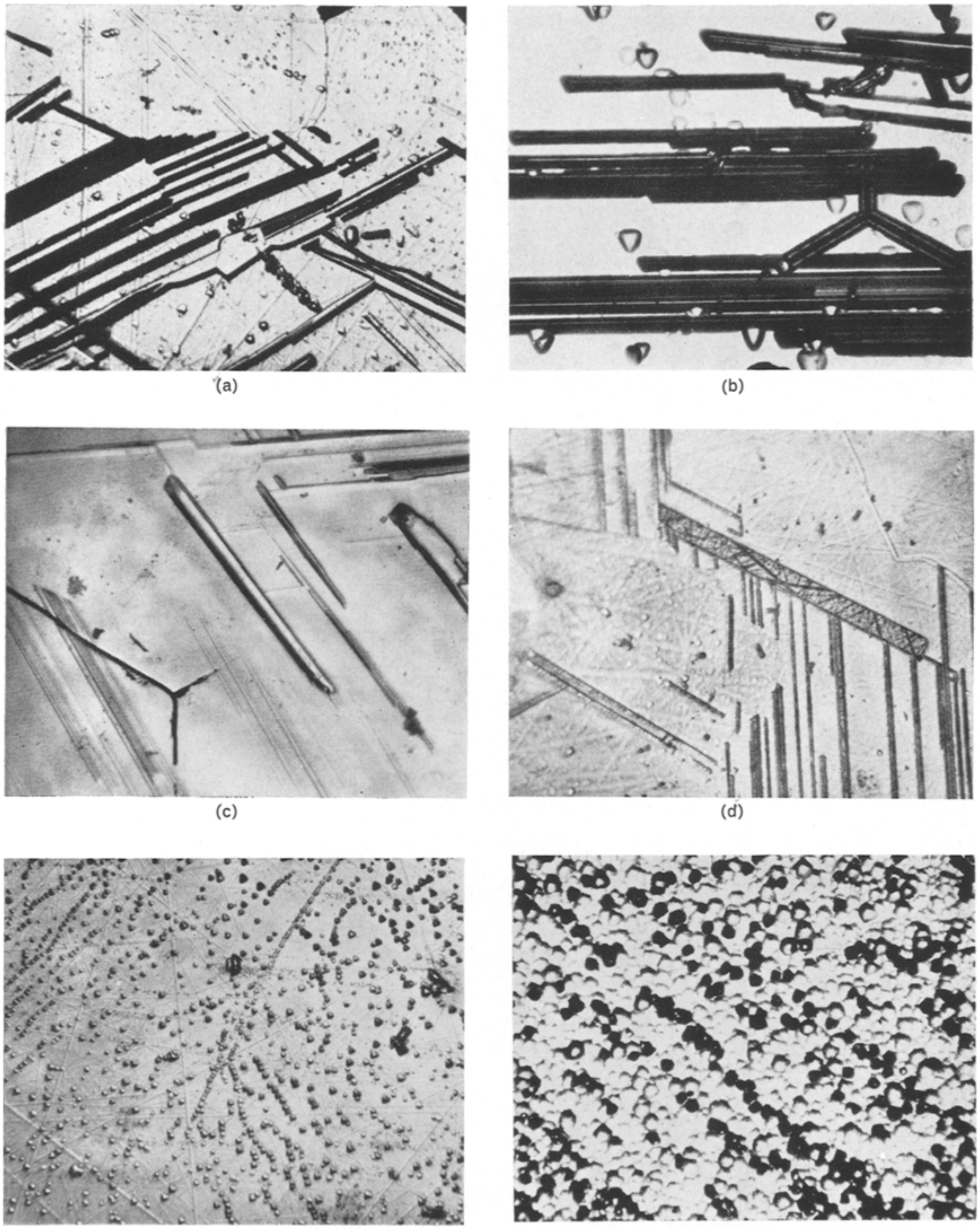
A systematic study of specimens etched in the various reagents was carried out in the electron microscope and the following observations made. Reagents 1 to 3 all produced pits which were associated with a dislocation intersecting the Ga{1 1 1} surface of the specimen at the apex of the pit. This is shown in fig. 2a: here the dislocation is the normal one for the sphalerite lattice (16) with the axis along ⟨1 1 0⟩ and Burgers vector $a/2$ ⟨1 1 0⟩. The triangular etch pit in the {1 1 1} surface is delineated by the extinction contours produced by the increasing thickness of the foil away from the apex of the pit. In the case of all three reagents containing the chemical component HCl, such pits were always associated with dislocations as shown in the micrograph.

In fig. 2b is shown the high density of dislocation loops punched in by surface damage acquired from the polishing wheel. The axes of these dislocations lay along ⟨1 1 0⟩ in the foil, independent of the direction of motion of the particle giving rise to them. In the absence of a final chemical polish after polishing on $\frac{1}{4}$ μm diamond compound, such bands of dislocations were invariably seen under the electron microscope. The data confirm the postulate made concerning the nature of the shallow channels seen after etching; the fine structure of these channels is the result of damage-induced dislocations being etched away; this is very quickly done since the depth of damage in most instances is only a fraction of a micron.

Within the lower end of the ingot, etching had indicated that polygonisation could be occurring during the growth cycle. Fig. 2c shows the interaction of two sub-boundaries, the misorientation between the top and bottom of the micrograph produced by the dislocations was found by Kikuchi line shift to be ≈ 0° 10′. The dislocations making up the sub-boundaries were again found by diffraction techniques to be ⟨1 1 0⟩ type.

3.2.2. Twin Boundaries

A typical set of twins is shown in fig. 3a. The contrast from various parts of the twins is characteristic of normal overlapping stacking faults in this structure. That the structure is twinned is shown by the extra spots in fig. 3b about the (220) reflections. The twin plane



(a) (b) (c) (d) (e) (f)

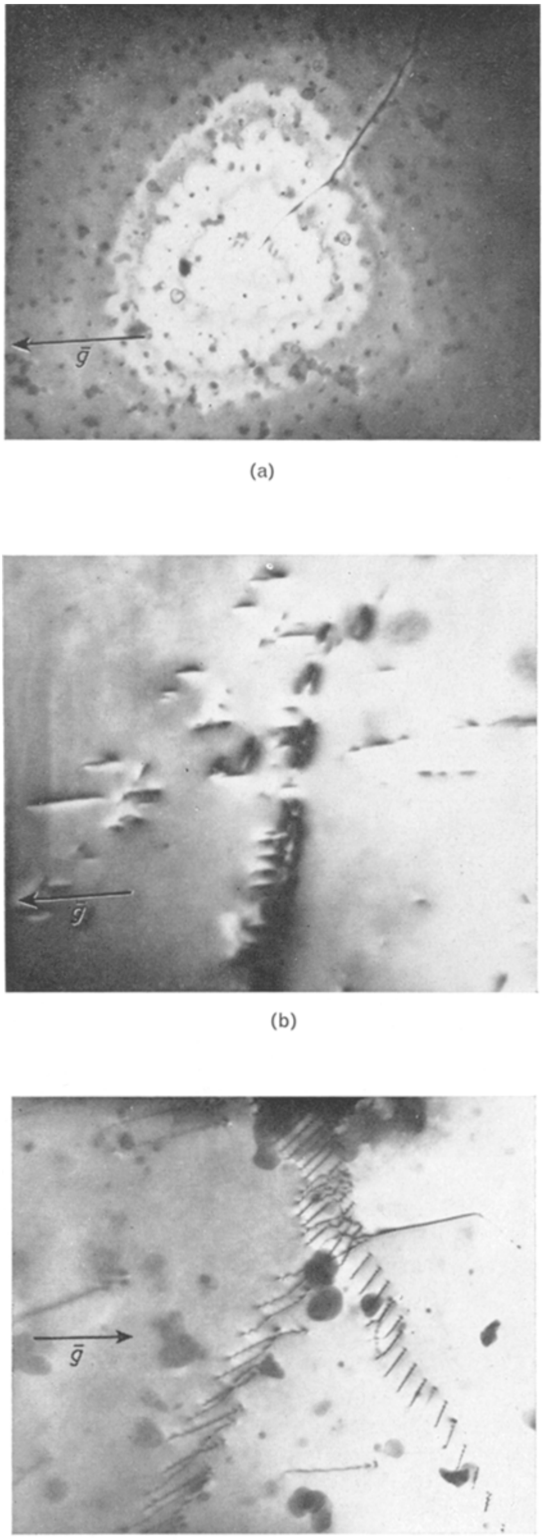
Figure 1 (a) Ga (111) face of GaP etched with reagent 1 for 5 min showing dislocation etch pits, sub-boundaries and twin lamellae (× 200). (b) Twin lamellae on Ga (111) face (× 600); compare with (c). (c) Twin lamellae revealed by etching on P ($\bar{1}\bar{1}\bar{1}$) face of GaP (× 600). The three-pointed star corresponds to the similar feature in (b). (d) Delineation of twin lamellae and sub-boundaries by reagent 4. Surface damage is apparently greater within twinned region. Notice how twins have one end common with a sub-boundary (× 200). (e) Etch pits and surface damage channels, pits beginning to align preparatory to forming subgrains. Structure produced by 5 min immersion in reagent 1 after final polish on $\frac{1}{4}$ μm diamond compound (× 200). (f) Etch pits and surface faceting produced on Ga (111) face after a 6 μ alumina lapp with 15 min in aqua regia (× 350).

intersects the $\{111\}$ foil along a $[220]$ direction. No extra reflections are seen associated with the reflections arising from planes perpendicular to the line of intersection of the twin with the foil plane. For example with a (111) foil normal, using the formulae for crystals with orthogonal axes [17], twinning on the $(\bar{1}11)$ plane causes the $(0\bar{2}2)$ reflection to correspond to $(02\bar{2})$. A detailed interpretation of the (111) reciprocal lattice of the twinned sphalerite structure has been carried out by Holt [18].

Quite frequently twin lamellae were found in pairs such as those shown in fig. 3c. Dislocations in the twin bands were often grouped together when the bands were closely associated, indicating interaction between dislocations in the twin bands, causing pile-ups. In this case (fig. 3c), the pile-ups alternate between the twin lamellae. The pile-ups were also observed where interaction had taken place with matrix dislocations. Such microtwins have been reported in copper where they had interacted with a coherent twin boundary after deformation of the foil [19]. Because of this already existing detailed diffraction study carried out for this type of defect, it will suffice to say that here the observed diffraction contrast was consistent with the twin lamellae being formed by $a/6\ \langle 112\rangle$ type shear vectors in those $\{111\}$ planes that were not the growth planes; twinning did not occur on the growth plane. The twinned regions may be made up of intrinsic fault layers on each $\{111\}$ plane or extrinsic faults on every other $\{111\}$ plane [20]. However, the nature of the faults has not been determined in the work reported here.

4. Discussion

The etching results, coupled with the results obtained from the electron microscope study, confirm the one-to-one correspondence between surface structure and substructural defects. This study has shown that aqua regia is a suitable reagent for revealing the dislocated substructure of gallium phosphide, although it is slow in its



(a)

(b)

(c)

Figure 2 (a) Transmission electron micrograph of an *a*/2 $\langle 110\rangle$ type dislocation emerging on a Ga $\{111\}$ face at the apex of an etch pit produced with aqua regia; $\bar{g} = 02\bar{2}$ ($\times$ 12,000). (b) TEM of dislocation loops produced by surface damage, surface unetched; $\bar{g} = 0.2\bar{2}$ ($\times$ 21,000). (c) TEM of the intersection of two sub-boundaries in the polygonised region of an ingot, majority dislocations have $\bar{\mathbf{b}} = a/2\langle 110\rangle$; $\bar{g} = 02\bar{2}$ in subgrain marked ($\times$ 21,000).

action. The dislocation morphology in a bulk ingot changes from the seed to the tail end of an ingot, the density of dislocations increasing by over two orders of magnitude at the tail end. It is well known that the crystal perfection in GaAs decreases from the seed to the tail and this has been attributed to impurity segregation effects [21, 22]. Impurity segregation can be detected in GaP since fairly pure material transmits light in the yellow end of the optical spectrum, while heavy segregation leads to opacity. Dislocation climb and alignment into subgrain-boundaries as growth proceeds suggests that GaP carries a high point defect concentration which assists this phenomenon. The phase width of GaAs has been determined to be quite small [23]. Therefore, the range of non-stoichiometry is small, there are fewer point defects and there is not the same tendency to polygonise at an early stage as there is in GaP. On this basis the substructural behaviour suggests that GaP may be able to retain a higher degree of non-stoichiometry than GaAs.

From the previous work on deformation and the nature of dislocations in structure of similar type [24, 25] it is highly likely that the stacking fault energy of GaP is in the medium to high range and therefore twinning as a mode of deformation is not to be expected under normal circumstances. It has been found that twinning is facilitated under hydrostatic pressure with an increased temperature [26] and also that rapid quenching produces twinning in Al_2O_3. A combination of these effects could have given rise to the twins in GaP; although the hydrostatic pressure is relatively small in the high-pressure Czochralski puller [2], the quenching of the ingot is probably quite rapid owing to the high pressure of inert gas in contact with the crystal emerging from the crucible.

The association of twins and sub-boundaries suggests that the twinning dislocations may arise from the dissociation of dislocations in the sub-boundary, since the majority of dislocations in sub-boundaries were found to be $a/2\ \langle 1\,1\,0 \rangle$, and such dislocations may dissociate in the classical manner of Cottrell and Bilby [27] to produce the

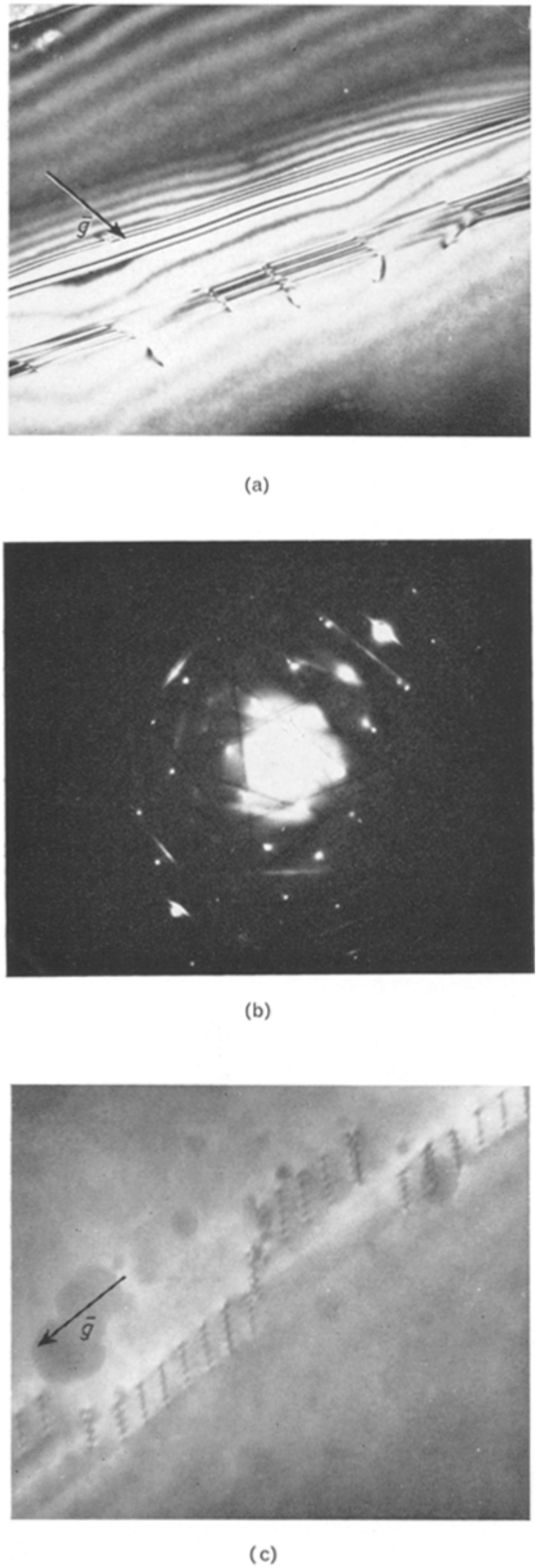


Figure 3 (a) Transmission electron micrograph of twin lamellae on the (111) plane in GaP; $\bar{g} = \bar{2}02$ (× 12,000). (b) Selected area diffraction pattern of twinned GaP showing matrix and twin reflections for a {111} plane normal to the electron beam. (c) Twin lamellae showing alternating pile-up behaviour of partial dislocation fault contrast absent; $\bar{g} = \bar{2}02$ (× 21,000).

$a/6 \langle 112 \rangle$ twinning dislocations. It has not been possible so far to test this thesis as no suitable thin films containing a sub-boundary twin interaction have been obtained. The tips of the twins were often blunted and some twins were quite extensive; Cahn [28] found that this type of blunting occurs in uranium to achieve the lowest surface energy, just as in annealing twins. Densely packed twin lamellae tend to join up laterally forming a new grain. For this phenomenon it has been postulated [29] that in uranium, sub-boundary migration causes some change in the twin matrix orientation relationship, leading to an increase in free energy of the twin matrix interface. Such a process is a possibility in GaP since there is a high incidence of sub-boundaries in the twinned regions of the ingot. A reduction of free energy is caused by advance of the twin boundaries.

5. Summary and Conclusions

Etching of slices on $\{111\}$ oriented gallium phosphide grown by the high-pressure Czochralski technique in reagents containing the chemical component HCl show well-defined structures, and in particular triangular etch pits are produced where a grown-in dislocation intersects the Ga$\{111\}$ face. Dislocations induced by surface damage are revealed as shallow etch channels containing a fine internal structure. Aqua regia was found to be a suitable reagent for revealing substructural defects; however, reagent 1 is recommended over aqua regia for its speed of action. Although GaP is not expected to have a low stacking fault energy, it has been shown that this material does twin and this was attributed to the severe growth conditions. The high incidence of sub-boundary formation in the last portions of an ingot to solidify indicates a high point defect concentration and hence an appreciable deviation from stoichiometry. Annealing of the substructure takes place during the growth cycle.

Acknowledgements

Gratitude is extended to P. Gurnell, S. Bass and their colleagues in the Ministry of Defence Services Electronics Research Laboratories for supplying the crystals of gallium phosphide and their assistance and co-operation. One of us (D.L.) was in receipt of an SRC research grant.

References

1. S. J. BASS and P. E. OLIVER, *J. Cryst. Growth* **34** (1968) 286.
2. S. J. BASS, P. E. OLIVER, and J. E. BIRKBECK, *ibid* **2** (1968) 169.
3. R. A. LOGAN, H. G. WHITE, and F. A. TRUMBORE, *J. Appl. Phys.* **38** (1967) 2500.
4. R. H. SAUL, *J. Electrochem. Soc.* **115** (1968) 1184.
5. M. GERSHENZON and R. M. MIKULYAK, *J. Appl. Phys.* **35** (1964) 2132.
6. M. M. COHEN and F. D. BEDARD, *ibid* **39** (1968) 75.
7. C. J. BUIOCCHI, *ibid* **38** (1967) 1980.
8. D. LAISTER and G. M. JENKINS, *Solid State Electron*, to be published.
9. G. R. BOOKER, *Phil. Mag.* **11** (1965) 1007.
10. M. S. ABRAHAMS and C. J. BUIOCCHI, *J. Phys. Chem. Solids* **28** (1967) 927.
11. A. STEINEMANN and U. ZIMMERLI, *Solid State Electron* **6** (1963) 597.
12. T. H. BLEWITT, R. R. COLTMANN, C. E. KLABUNDE and T. S. NOGGLE *J. Appl. Phys.* **28** (1957) 639.
13. G. L. PEARSON and F. L. VOGEL, *Prog. in Semiconductors* **6** (1962) 1.
14. A. T. CHURCHMAN, G. A. GEACH, and J. WINTON, *Proc. Roy. Soc. (London)* **A238** (1956) 194.
15. E. BIEDERMANN and K. BRACK, *J. Electrochem. Soc.* **113** (1966) 1088.
16. J. HORNSTRA, *J. Phys. Chem. Solids* **5** (1958) 129.
17. P. B. HIRSCH, A, HOWIE, R. B. NICHOLSON, D. W. PASHLEY and M. J. WHELAN, "Electron Microscopy of Thin Crystals" (Butterworth, London, 1965) p. 142.
18. D. B. HOLT, *J. Mater. Sci.* **4** (1969) 935.
19. S. MAHAJAN, D. E. BARRY and B. L. EYRE, *Phil. Mag.* **21** (1970) 43.
20. J. A. VENABLES, "Deformation Twinning", Met. Soc. Conf. AIME **25** (Gordon and Breach, London and NY, 1964).
21. M. S. ABRAHAMS, C. J. BUIOCCHI and J. J. TIETJEN, *J. Appl. Phys.* **38** (1967) 760.
22. D. LAISTER and G. M. JENKINS, *J. Mater. Sci.* **3** (1968) 584.
23. M. E. STRAUMANIS and C. D. KIM, *Acta Cryst.* **19** (1965) 256.
24. G. R. BOOKER and R. STICKLER, *Acta Met.* **10** (1962) 993.
25. D. LAISTER, PhD Thesis, University of Wales (1969) 192.
26. M. V. KLASSEN-NEKLYUDOVA, "Mechanical Twinning of Crystals" (Consultants Bureau, New York, 1964) p. 69.
27. A. H. COTTRELL and B. A. BILBY, *Phil. Mag.* **42** (1951) 573.
28. R. W. CAHN, "Deformation Twinning", Met Soc. Conf., AIME **25** (Gordon and Breach, London and NY, 1964) p. 19.
29. D. CALAIS, P. LACOMBE and N. SIMENEL, *Mem. Sci. Rev. Metallurgie* **56** (1959) 261.

Received 6 May and accepted 22 June 1970